

PCT

WORLD INTELLIGENT PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C07C 15/107, 2/66		A1	(11) International Publication Number: WO 00/23404
			(43) International Publication Date: 27 April 2000 (27.04.00)
(21) International Application Number: PCT/US99/24274		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 19 October 1999 (19.10.99)		Published <i>With international search report.</i>	
(30) Priority Data: 09/175,078 19 October 1998 (19.10.98) US			
(71) Applicant: HUNTSMAN PETROCHEMICAL CORPORATION (US/US); Russell R. Stolle, 7114 North Lamar Boulevard, Austin, TX 78746 (US).			
(72) Inventor: ANANTANENI, Prakasa, Rao; 13019 Partridge Bend Drive, Austin, TX 78729 (US).			
(74) Agent: O'KEEFE, Robert, M.; O'Keefe, Egan & Petermar, LLP, 1101 Capital of Texas Highway South, Building C, Suite 200, Austin, TX 78746 (US).			
(54) Title: ALKYLATION OF BENZENE TO FORM LINEAR ALKYLBENZENES USING FLUORINE-CONTAINING MORDENITES			
(57) Abstract			
<p>This invention is directed to a fluorine-containing mordenite catalyst and use thereof in the manufacture of linear alkylbenzene (LAB) by alkylation of benzene with a paraffin. The paraffin may have from about 10 to 14 carbons. The fluorine-containing mordenite is prepared typically by treatment with an aqueous hydrogen fluoride solution. The benzene alkylation may be conducted using reactive distillation. This invention is also directed to a process for production of LAB having a high 2-phenyl isomer content by combining LAB product from the fluorine-containing mordenite product from a conventional LAB alkylation catalyst such as hydrogen fluoride.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	IS	Iceland	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MJ	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TK	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IR	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NI	Netherlands	VN	Viet Nam
CG	Congo	KP	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Lithuania	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		

D scription

5

10

15

20

25

30

35

40

45

50

55

5

1

2 **ALKYLATION OF BENZENE TO FORM LINEAR ALKYLBENZENES**
10 **USING FLUORINE-CONTAINING MORDENITES**

3

4

5 **BACKGROUND OF THE INVENTION**

6

15

7 This invention generally relates to the alkylation of benzene with paraffins using
8 mordenite catalysts.

9

20

10 Linear alkylbenzenes (LAB's) having long chains (typically 10-14 carbons) are
11 commonly used, commercial products. LAB's are commonly sulfonated to thereby produce
12 surfactants.

13

25

14 Typically, LAB's are manufactured commercially using classic Friedel-Crafts chemistry,
15 employing catalysts such as aluminum chloride, or using strong acid catalysts such as hydrogen
16 fluoride, for example, to alkylate benzene with paraffins. While such methods produce high
17 conversions, the selectivity to the 2-phenyl isomer is low, generally being about 30% or less.
18 LAB's with a high percentage of the 2-phenyl isomer are highly desired because such
19 compounds when sulfonated have long "tails" which provide enhanced solubility and detergent
20 properties.

35

21 **SUMMARY OF THE INVENTION**

23

40

24 It has now been recognized that a need exists for a method of LAB production having
25 high substrate paraffin conversion, high selectivity to 2-phenyl isomer LAB, and employing a
26 catalyst having long lifetimes and easy handling. This invention provides a solution to one or
27 more of the problems and disadvantages described above.

28

45

29 It has also been found that the catalyst of this invention may be used in combination
30 with an existing aluminum chloride or hydrogen fluoride alkylation facility to afford LAB

50

55

5

-2-

10

15

20

25

30

35

40

45

50

55

1 having a higher 2-phenyl isomer content than would otherwise be available from such plant.
2 Thus, an existing facility may be retrofitted to include one or more reactors containing the
3 fluorine-containing mordenite of this invention. In this manner, a slip stream of reactants may
4 be sent to the mordenite with effluent therefrom being introduced back into the conventional
5 alkylation system. This embodiment has several advantages. For example, the cost of capital is
6 minimized since conventional equipment will already be in place. Also, the retrofitted plant can
7 produce higher 2-phenyl isomer LAB at the discretion of its operator, depending on need. That
8 is, the plant need not produce strictly high 2-phenyl isomer LAB and can instead produce high
9 2-phenyl isomer at its discretion. In one embodiment, a slip stream of reactant is drawn and
10 sent to one or more reactors containing fluorine-containing mordenite catalyst. The effluent
11 from the fluorine-containing mordenite reactor may then be combined with effluent from the
12 HF or aluminum chloride reactor to provide a product having a higher level of 2-phenyl isomer
13 LAB than would otherwise be present in product from an HF or aluminum chloride reactor.

14

15 This invention, in one broad respect, is a process useful for the production of
16 monoalkylated benzene, comprising contacting benzene with an paraffin containing from about
17 8 to about 30 carbons in the presence of fluorine-containing mordenite under conditions such
18 that linear monoalkylated benzene is formed.

19

20 In another broad respect, this invention is a process for the production of linear
21 alkylbenzene, comprising:

22 contacting benzene and an paraffin having about 8 to about 30 carbons in the presence
23 of a fluorine-containing mordenite to form a first linear alkylbenzene stream;

24 contacting benzene and an paraffin having about 8 to about 30 carbons in the presence
25 of a conventional linear alkylbenzene alkylation catalyst to form a second linear alkylbenzene
26 stream;

27 combining the first linear alkylbenzene stream and the second linear alkylbenzene
28 stream form a third linear alkylbenzene stream, as well as the product made from this process.

29

5

-3-

10

1 In another broad respect, this invention is a process useful for the production of linear
2 alkylbenzene, comprising:
3 combining a product from a conventional linear alkylbenzene alkylation reactor with a
4 product from a linear alkylbenzene alkylation reactor containing fluorine-containing
5 mordenite.

15

6
7 In yet another broad respect, this invention is a process for the production of linear
8 alkylbenzene, comprising:

20

9 dehydrogenating a paraffin to form an paraffin;
10 sending a primary feed stream of benzene and the paraffin through a conduit to a
11 conventional linear alkylbenzene alkylation reactor;

25

12 contacting the primary feed stream in the conventional linear alkylbenzene alkylation
13 reactor with a conventional linear alkylbenzene alkylation catalyst under conditions effective
14 to react the benzene and paraffin to form a first linear alkylbenzene product;

30

15 withdrawing a portion of the primary feed stream from the conduit and contacting the
16 portion with a fluorine-containing mordenite under conditions effective to react the benzene
17 and paraffin to form a second linear alkylbenzene product;

35

18 combining the first and second linear alkylbenzene products to form a crude linear
19 alkylbenzene stream;
20 distilling the crude linear alkylbenzene stream in a first distillation column to separate
21 benzene that did not react and to form a benzene-free linear alkylbenzene stream;
22 optionally distilling the benzene-free linear alkylbenzene stream in a second
23 distillation column to separate any paraffin and to form a linear alkylbenzene stream;
24 distilling the second paraffin free alkylbenzene stream in a third distillation column to
25 provide an overhead of a purified linear alkylbenzene product and removing a bottoms stream
26 containing any heavies.

40

27
28 In another broad respect, this invention is a process useful for the production of
29 monoalkylated benzene, comprising introducing a feed comprising paraffin having about 8 to
30 about 30 carbons and benzene into a fluorine-containing mordenite catalyst bed under

50

55

5

-4-

10

1 conditions such that monoalkylated benzene is produced, allowing benzene, paraffin, and
2 monoalkylated benzene to descend (fall) into a reboiler from the catalyst bed, removing
3 monoalkylated benzene from the reboiler, and heating the contents of the reboiler such that
4 benzene refluxes to further contact the fluorine-containing mordenite.

15

5
6 In another broad aspect, this invention relates to mordenite useful for alkylating benzene
7 with paraffin having a silica to alumina molar ratio of about 10:1 to about 100:1; wherein the
8 mordenite has been treated with an aqueous hydrogen fluoride solution such that the mordenite
9 contains from about 0.1 to about 4 percent fluorine by weight.

20

10
11 In another broad respect, this invention is a method useful for the preparation of
12 fluorine-containing mordenite, comprising contacting a mordenite having a silica to alumina
13 molar ratio in a range from about 10:1 to about 100:1 with an aqueous hydrogen fluoride
14 solution having a concentration of hydrogen fluoride in the range of from about 0.1 to about 10
15 percent by weight such that the mordenite containing fluorine is produced, collecting the
16 fluorine-containing mordenite by filtration, and drying.

17

30
18 The fluorine treated mordenite catalyst advantageously produces high selectivities to the
19 2-phenyl isomer in the preparation of LAB, generally producing selectivities of about 70
20 percent or more. Also, the fluorine treated mordenite enjoys a long lifetime, preferably
21 experiencing only a 25 percent or less decrease in activity after 400 hours on stream. A process
22 operated in accordance with the apparatus depicted in FIGS. 1 and 2 has the advantage that
23 rising benzene from the reboiler continuously cleans the catalyst to thereby increase lifetime of
24 the catalyst. In addition, this invention advantageously produces only low amounts of
25 dialkylated benzene, which is not particularly as useful for detergent manufacture, as well as
26 only low amounts of tetralin derivatives.

27

40
28 Certain terms and phrases have the following meanings as used herein.
29

50

55

5

-5-

10

1 "Meq/g" means milliequivalents of titratable acid per gram of catalyst, which is a unit
2 used to describe acidity of the catalysts. Acidity is generally determined by titration with a
3 base, as by adding excessive base, such as sodium hydroxide, to the catalyst and then back
4 titrating the catalyst.

15

5
6 "Conv." and "Conversion" mean the mole percentage of a given reactant converted to
7 product. Generally, paraffin conversion is about 95 percent or more in the practice of this
8 invention.

20

9
10 "Sel." and "Selectivity" mean the mole percentage of a particular component in the
11 product. Generally, selectivity to the 2-phenyl isomer is about 70 or more in the practice of this
12 invention.

25

13
14 The mordenite catalyst of the present invention is useful as a catalyst in the production
15 of LAB's in accordance with the process of manufacturing LAB's of this invention. LAB is
16 useful as starting material to produce sulfonated LAB, which itself is useful as a surfactant.

30

17
18 **BRIEF DESCRIPTION OF THE DRAWINGS**

19

35

20 FIG. 1 shows a representation of a first continuous reactive distillation column
21 employed in the practice of this invention.

40

22 FIG. 2 shows a representation of a second continuous reactive distillation column
23 employed in the practice of this invention.

45

25
26 FIG. 3 shows a representative process scheme for one embodiment of this invention
27 where a conventional LAB alkylation reactor is shown in combination with a fluorine-
28 containing mordenite reactor of this invention wherein a slip stream of reactant to the
29 conventional reactor is sent to the mordenite reactor and wherein the flow of high 2-phenyl

50

55

5

-6-

1 isomer LAB from the mordenite reactor may be adjusted to vary the 2-phenyl isomer LAB
2 content of the effluent from the conventional LAB alkylation reactor.

10

4 FIG. 4 shows another representative process scheme for one embodiment of this
5 invention where a first conventional LAB alkylation reactor is shown in combination with a
6 fluorine-containing mordenite reactors of this invention wherein a slip stream of reactant to the
7 conventional reactor is sent to one or both of a pair of mordenite reactor and wherein the
8 effluent from the first LAB alkylation reactor and the effluent from the one or both mordenite
9 reactors are combined and flowed into a second conventional LAB alkylation reactor.

10

11 DETAILED DESCRIPTION OF THE INVENTION

12

13 *Catalyst Preparation and Properties*

14

15 The catalyst of this invention is a fluorine-containing mordenite. Mordenite is a type of
16 zeolite. The catalyst of this invention is prepared from hydrogen mordenite (typically having
17 0.1 percent or less of sodium) having a silica-alumina molar ratio of from about 10:1 to about
18 100:1. More typically, the starting mordenite has a silica/alumina molar ratio of from about
19 10:1 to about 50:1. The starting hydrogen mordenite, which is commonly available
20 commercially, is treated with an aqueous solution of hydrogen fluoride ("HF") to produce the
21 active, long-life and highly selective catalyst of the invention. In the course of such HF
22 treatment, as well as during subsequent calcination of said HF-treated mordenite, the
23 silica/alumina molar ratio typically increases. The finished catalysts of this invention show a
24 fluorine content of from about 0.1 to about 4 percent by weight, more typically about 1 percent.

25

26 While not wishing to be bound by theory, it is believed that the HF reacts with sites
27 where -Si-O-Al- linkages occur such that the linkage is broken with fluorine becoming bonded
28 to the Al such that -Si-OH and F-Al- groups form. This is believed to decrease the total
29 Bronsted acid sites and increase the strength of the remaining acid sites in the mordenite and is

50

55

5

-7-

1 believed to stabilize the acidity of the mordenite such that the mechanisms which degrade
2 performance during LAB production, such as coke build-up, are retarded.

10

3
4 The aqueous solution used to treat the mordenite may contain a range of HF
5 concentrations. Generally, the HF concentration is a minimum of about 0.1 percent by weight.
6 Below such minimum concentration, the effect of the fluorine treatment significantly decreases,
7 resulting in the undesirable need for repeated treatments. Generally, the HF concentration on
8 the upper end is about 10 percent by weight or less. Above a concentration of about 10 percent
9 by weight, the HF is so concentrated that it is difficult to prevent HF from destroying the
10 crystallinity of the mordenite, thereby detrimentally affecting its efficacy as a catalyst for LAB
11 production.

20

12
13 The aqueous HF solution may be prepared by diluting commercially available 48% HF
14 solutions to the desired concentration. Alternatively, HF can be sparged into water to provide
15 an aqueous HF solution.

25

16
17 Typically, the treatment is carried out by adding mordenite powder or pellets to a stirred
18 aqueous HF solution at a temperature of from about 0°C to about 50°C. The stirring and
19 contacting is continued for a time sufficient to achieve the desired level of fluorine in the
20 mordenite. This time may vary depending on factors such as HF concentration, amount of HF
21 solution relative to the amount of mordenite being treated, speed of agitation is employed, and
22 temperature. After treatment, the mordenite can be recovered by filtration, and then dried. It is
23 also possible to impregnate the mordenite to incipient wetness with a given HF solution, as well
24 as to treat the mordenite with gaseous hydrogen fluoride. Preferably said fluoride-treated
25 mordenite would be calcined in air prior to use in alkylation service. The preferred calcination
26 temperature would be in the range from about 400°C to about 600°C. Alternative mordenite
27 fluorinating agents to hydrofluoric acid and hydrogen fluoride include ammonium fluoride,
28 fluorided silicon compounds and fluorided hydrocarbons.

40

29

50

55

5

-8-

10

1 The HF-treated mordenite of this invention generally has about 0.1 percent by weight or
2 more of fluorine based on the total weight of the mordenite. Typically, the fluorine-containing
3 mordenite contains about 4 percent by weight or less fluorine. The fluorine-containing
4 mordenite most typically contains about 1 percent by weight of fluorine.

15

5 The mordenite can be used in the practice of this invention as a powder, in pellet
6 form, as granules, or as extrudates. The mordenite can be formed into pellets or extrudates
7 using binders well known to those of skill in the art, such as alumina, silica or mixtures
8 thereof.

20

10 *Reactants for LAB Production*

11

25

12 In the practice of this invention, benzene is alkylated with paraffin to form LAB. These
13 reactants can be handled and purified as is generally performed by those of skill in the art. In
14 this regard, it is preferred that the reactants are water and alcohol free. The paraffins employed
15 in the practice of this invention have from about 8 to about 30 carbons, preferably from about
16 10 to about 14 carbons, such as is available commercially or produced as dehydrogenated
17 paraffin feed stocks. It is preferred that the paraffin be monounsaturated. It is most preferred
18 that the paraffin be an alpha-paraffin containing a terminal ethylenic unit.

30

19

20 Commonly, said paraffins would be available in a paraffin media of the same carbon
21 range. Paraffins in the 10 to 14 carbon number range would typically be available from C₁₀ to
22 C₁₄. Paraffin dehydrogenation in a C₁₀ to C₁₄ paraffin mixture having an paraffin content of 5 to
23 20%. Often, the paraffin content of said paraffin-paraffin mixture would be 8 to 10 weight %.

35

24

25 The 2-phenyl isomer of the LAB produced in accordance with this invention is of
26 formula:

45

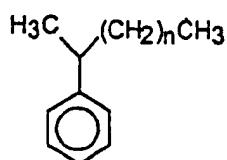
50

55

5

-9-

10

1
2
3
4
5
6

15

7
8
9

wherein n is from about 5 to about 17 and preferably from about 7 to about 11.

20

10 *Process Conditions, Procedures, and Apparatus*

11

25

12 The process of this invention can be carried out using the continuous reactive distillation column depicted in FIG. 1. In FIG. 1, a feed mixture of benzene and paraffin, generally at a benzene-to-paraffin molar ratio range of about 1:1 to 100:1 flows from feed pump 10 to feed inlet 14 via line 12. The feed mixture falls to packed mordenite catalyst bed 32 where alkylation in the presence of the fluorine-containing mordenite occurs. Alternatively, while not depicted in FIG. 1, the benzene and paraffin can be introduced separately into the bed with mixing occurring in the bed, or the reactants can be mixed via an in-line mixer prior to introducing the reactants into the catalyst bed, or the reactants can be injected separately above the bed with mixing affected by use of standard packing above the bed, or the reactants can be sparged into the chamber above the bed. The catalyst bed 32 depicted in FIG. 1 for laboratory scale may be made of two lengths of 1.1 inch internal diameter tubing, the lengths being 9.5 inches and 22 inches. In the catalyst bed 32, the falling feed mixture also contacts rising vapors of unreacted benzene which has been heated to reflux in reboiler 42 by heater 40. Such rising vapors pass over thermocouple 38 which monitors temperature to provide feedback to heater 40. The rising vapors of benzene and/or paraffin also pass through standard packing 36 (e.g., 7.5 inches of goodloe packing). The rising vapors heat thermocouple 30 which connects to bottoms temperature controller 28 which activates heater 40 when temperature drops below a set level.

35

40

45

29

50

55

5

-10-

10

1 Prior to startup, the system may be flushed with nitrogen which enters via line 54 and
2 which flows through line 58. After startup, a nitrogen blanket is maintained over the system.
3 Also prior to startup and during nitrogen flush, it may be desirable to heat catalyst bed 32 so as
4 to drive off water from the fluorine-containing mordenite.

15

20

5 Residual water from the feed mixture or which otherwise enters the system is collected
6 in water trap 24 upon being liquefied at condenser 21 (along with benzene vapor). If the feed is
7 very dry (free of water) the water trap 24 may not be needed. Removing water leads to longer
8 catalyst lifetime. Hence, the water trap 24 is optional. The same applies to FIG. 2. Condenser
9 21 is cooled via coolant such as water entering condenser 21 via port 22 and exiting via port 20.
10 As needed, water in water trap 24 may be drained by opening drain valve 26.

12

25

13 As needed, when LAB content in reboiler 42 rises to a desired level, the bottoms LAB
14 product may be removed from the system via line 47, using either gravity or bottoms pump 48
15 to withdraw the product. When product is so withdrawn, valve 44 is opened.

35

40

16 In FIG. 1, dip tube 46, which is optional, is employed to slightly increase the pressure in
17 reboiler 42 to thereby raise the boiling point of benzene a degree or two. Likewise, a pressure
18 generator 56 may be optionally employed to raise the pressure of the system. Other standard
19 pressure increasing devices can be employed. Pressure can thus be increased in the system such
20 that the boiling point of benzene increases up to about 200°C.

22
23 In FIG. 1, control mechanisms for heat shutoff 50 and pump shutoff 52 are depicted
24 which serve to shut off heat and pump if the liquids level in the system rises to such levels.
25 These control mechanisms are optional and may be included so that the catalyst bed does not
26 come into contact with the bottoms of the reboiler. Line 60 connects pump shutoff 52 to the
27 system above condenser 21.

45

28
29 In the practice of this invention in the alkylation of benzene, a wide variety of process
30 conditions can be employed. In this regard, the temperature in the catalyst bed may vary

50

55

5

-11-

10

15

20

25

30

35

40

45

50

55

1 depending on reactants, rate of introduction into the catalyst bed, size of the bed, and so forth.
2 Generally, the bed is maintained at the reflux temperature of benzene depending on pressure.
3 Typically, the temperature of the catalyst bed is above about 70°C, and most likely about 78°C
4 or more in order to have reasonable reaction rates, and about 200°C or less to avoid degradation
5 of reactants and products and to avoid deactivation of the catalyst by coke build-up. Preferably,
6 the temperature is in the range from about 80°C to about 140°C. The process may be operated
7 at a variety of pressures during the contacting step, with pressures of about atmospheric most
8 typically being employed. When the process is operated using a system as depicted in FIGS. 1
9 and 2, the reboiler temperature is maintained such that benzene and paraffin vaporize, the
10 temperature varying depending on paraffin, and generally being from about 80°C to about
11 250°C for paraffins having 10 to 14 carbons. The composition of the reboiler will vary over
12 time, but is generally set initially to have a benzene paraffin ratio of about 5:1, with this ratio
13 being maintained during the practice of this invention. The rate of introduction of feed into the
14 catalyst bed may vary, and is generally at a liquid hourly space velocity ("LHSV") of about
15 0.05 hr⁻¹ to about 10 hr⁻¹, more typically from about 0.05 hr⁻¹ to about 1 hr⁻¹. The mole ratio of
16 benzene to paraffin introduced into the catalyst bed is generally from about 1:1 to about 100:1.
17 In commercial benzene alkylation operations, it is common to run at mole ratios of from about
18 2:1 to about 20:1, which can suitably be employed in the practice of this invention, and to
19 charge said paraffins as an paraffin-paraffin mixture comprising 5% to 20% paraffin content.
20 Said paraffin-paraffin mixtures are normally generated commercially through dehydrogenation
21 of the corresponding paraffin starting material over a noble metal catalyst.

22
23 Another continuous reactive distillation apparatus is depicted in FIG. 2. In FIG. 2, the
24 feed mixture enters the reactor via feed inlet 114. The feed mixture falls through the column
25 into catalyst bed 132, wherein alkylation to form LAB occurs. A thermowell 133 monitors the
26 temperature of said catalyst bed 132. The catalyst bed 132 may be optionally heated externally
27 and is contained within 1-1/4 inch stainless steel tubing. Goodloe packing is positioned at
28 packing 136 and 137. LAB product, as well as unreacted benzene and paraffin, fall through
29 packing 136 into reboiler 142. In reboiler 142, electric heater 140 heats the contents of reboiler
30 142 such that heated vapors of benzene and paraffin rise from the reboiler 142 to at least reach

5

-12-

10

15

20

25

30

35

40

45

50

55

1 catalyst bed 132. As needed, the bottoms LAB product may be removed from reboiler 142 by
2 opening bottoms valve 144 after passing through line 147 and filter 145. Residual water from
3 the feed mixture, or which otherwise enters the system, may be condensed at condenser 121
4 which is cooled with coolant via outlet line 122 and inlet line 120. The condensed water falls to
5 water trap 124, which can be drained as needed by opening drain valve 126. Temperature in the
6 system is monitored via thermocouples 138, 130, and 165. The system includes pressure
7 release valve 166. A nitrogen blanket over the system is maintained by introduction of nitrogen
8 gas via inlet line 154. Level control activator 150 activates bottoms level control valve 151 to
9 open when the liquids level in the reboiler rises to the level control activator 150. Line 160
10 connects level control activator 150 to the system above condenser 121.

11

12 While the systems depicted in FIG. 1 and FIG. 2 show single catalyst bed systems, it
13 may be appreciated that multi-catalyst bed reactors are within the scope of this invention, as
14 well as multiple ports for inlet feeds, water traps, product removal lines, and so forth.
15 Moreover, the process may be run in batch mode, or in other continuous processes using
16 plugflow designs, trickle bed designs, and fluidized bed designs.

17

18 It is believed that as average molecular weight of paraffins increases, particularly when
19 the average number of carbons exceed 14, the selectivity and conversion to LAB, especially
20 LAB with the 2-isomer, may incrementally decrease. If desired, the product of the alkylation
21 using HF-treated mordenite may be sent to a second, finishing catalyst bed to improve yield.
22 This procedure is optional and is believed to be dependent on the needs and desires of the end
23 user. An example of such a second catalyst is HF-treated clay such as montmorillonite clay
24 having about 0.5% fluoride. Such a catalyst may also serve to lower the bromine number below
25 about 0.1, depending on conditions.

26

5

-13-

1 *Variable 2-phenyl Isomer Content of Product Using the Mordenite of this Invention In*
2 *Combination with Conventional LAB Alkylation*

10

3
4 The fluorine-containing mordenite of this invention generally produces LAB having
5 high 2-phenyl isomer content, such as higher than about 70%. Currently, LAB purchasers who
6 make detergents would prefer to use LAB having a 2-phenyl isomer content in the range from
7 about 30 to about 40 percent, but this level is not available in the marketplace. Conventional
8 LAB alkylation technology do not achieve these higher 2-phenyl isomer levels. HF, which is
9 currently the most widely used catalyst for production of LAB on a commercial scale, produces
10 about 16-18 percent of the 2-phenyl isomer in the product stream from the reactor. Aluminum
11 chloride, in contrast, produces about 26-28 percent of the 2-phenyl isomer. The present
12 inventors recognized that a need exists for a process which produces a 2-phenyl isomer product
13 in the desired range.

25

14

15 It has now been found that the mordenite of this invention can be used in combination
16 with conventional LAB alkylation catalysts, such as HF and aluminum chloride alkylation
17 catalysts. This may be affected by withdrawing a slip stream of reactant that is being sent to the
18 conventional LAB reactor, and directing the slip stream to the mordenite reactor. Since
19 conventional LAB catalysts produce product having a 2-phenyl isomer content much less than
20 that from mordenite of this invention, combining the products from each catalyst results in a
21 product having a higher 2-phenyl isomer content than that from the conventional LAB
22 alkylation catalyst. For example, while the catalyst of this invention typically produces a 2-
23 phenyl isomer content of 70% or more, a typical HF process produces about 16-18% of the 2-
24 phenyl isomer. By combining effluent from each catalyst at given proportions, the resulting
25 mixture will have any desired 2-phenyl isomer content in the range between the 2-phenyl
26 isomer contents of the HF catalyst product and the mordenite catalyst product. Thus, the levels
27 of 2-phenyl isomer may be adjusted by the amount of reactants sent to the mordenite catalyst
28 and/or by storing 2-phenyl isomer product from the mordenite catalyst for later mixing with the
29 product of from the conventional LAB alkylation catalyst to thereby achieve any desired level
30 of 2-phenyl isomer content in the final product. An advantage of this invention pertains to the

50

55

5

-14-

10

1 ability to retrofit an existing, conventional LAB system with a reactor containing fluorine-
2 treated mordenite of this invention. This enables existing users of the conventional LAB
3 technology to augment their existing facilities without interrupting their production. This
4 provides a considerable cost advantage to the producer.

15

6 The conventional LAB catalysts used most frequently are HF alkylation reactors and
7 aluminum chloride alkylation catalysts. Other alkylation catalysts include various zeolites,
8 alumina-silica, various clays, as well as other catalysts.

20

9
10 FIG. 3 depicts a representative, non-limiting scheme for practice of this invention
11 wherein the fluorine-treated mordenite is used in combination with a HF alkylation reactor to
12 afford LAB having high 2-phenyl isomer contents relative to that produced from the HF reactor
13 alone. The scheme of FIG. 3 is shown in the context of LAB alkylation based on a feed from a
14 paraffin dehydrogenation facility. Prior to this invention, the plant depicted in FIG. 3 would be
15 operated conventionally without use of mordenite reactor 220.

25

16
17 Thus, in conventional operation, fresh paraffin is fed to conventional dehydrogenation
18 apparatus 210 via line 211, with recycled paraffin being introduced from the paraffin column
19 250 via line 252. Dehydrogenated paraffin from the dehydrogenation apparatus 210 is then
20 pumped into a conventional alkylation reactor 230 containing conventional LAB catalyst,
21 such as HF, via conduit 214. The dehydrogenated paraffin feed may of course be supplied
22 from any provider. The source of dehydrogenated paraffin (paraffin) is not critical to the
23 practice of this invention. LAB product from alkylation unit 230 may thereafter be purified
24 by a series of distillation towers.

30

25
26 In this regard, alkylation effluent is delivered to a benzene column 240 by way of line
27 231. It should be appreciated that the alkylation product may be sent offsite for purification.
28 Further, the particular purification scheme used is not critical to the practice of this invention,
29 but is depicted in FIG. 3 as representative of a typical commercial operation. In FIG. 3,
30 unreacted benzene is distilled off from the crude LAB product. Benzene is then recycled to
31 the alkylation reactor 230. The benzene-free LAB crude product from the benzene column

40

45

50

55

5

-15-

10

1 240 is pumped through line 241 to paraffin column 250 where any paraffin present is distilled
2 off, with the distilled paraffin being recycled to paraffin dehydrogenation unit 210 via line
3 252. Paraffin-free crude LAB alkylate from the paraffin column 250 is transported to a
4 refining column 260 where purified LAB is distilled and removed via line 262. Heavies (e.g.,
5 dialkylates and paraffin derivatives) are withdrawn from refining column 260 via conduit
6 261.

15

7
8 In the practice of this invention, a fluorine-treated mordenite containing reactor 220 is
9 used in conjunction with the conventional alkylation reactor 230. In the embodiment of this
10 invention depicted in FIG. 3, a slip stream of benzene/dehydrogenated paraffin feed is taken
11 from line 214 and pumped through mordenite reactor 220 where high 2-phenyl isomer
12 production is achieved. LAB product from reactor 220, high in 2-phenyl isomer, is then
13 introduced back into line 214 via line 222. Alternatively mordenite reactor 220 may be fed
14 benzene and dehydrogenated paraffin (paraffin) directly, rather than by way of a slip stream
15 from line 221. In addition, effluent from reactor 220 may, in the alternative if no unreacted
16 paraffin is present, be sent directly to benzene column 240, for later combination with
17 conventional alkylation reactor 230 product or transported and tied into conduit 231, which
18 feeds benzene column 240. It should be appreciated that columns 240, 250, and 260 may be
19 maintained at conditions (e.g., pressure and temperature) well known to those of skill in the
20 art and may be packed with conventional materials if desired.

25

30

35

40

45

21
22 FIG. 4 depicts an alternative configuration to that shown in FIG. 3. In FIG. 4, dual
23 mordenite beds 320, 321 are used in conjunction with conventional alkylation reactors 330,
24 340. Conveniently, one of the mordenite reactors may be in operation while the other reactor
25 is down for catalyst regeneration. For example, during operation, paraffin feed
26 (dehydrogenated paraffin) is supplied via line 301, with benzene or other aromatic feed stock
27 being provided via line 302. The admixed reactants may flow to standard alkylation reactor
28 330 via line 304b after passing through heat exchanger 303. A portion of the mixed stream
29 may be withdrawn via line 304a for supply to the mordenite reactor. The extent of the mixed
30 feed stream being withdrawn may be varied depending on the desired level of 2-phenyl

50

55

5

-16-

10

1 isomer in the final product. In another embodiment, the product from the reactor containing
2 mordenite 320, 321 may be fed to the first alkylation reactor 330, particularly if the second
3 alkylation reactor 34 is not employed in the process.

20

25

4
5 The slip stream reactants may optionally be sent to dewatering unit 317 by application
6 of pump 306 after passing through heat exchanger 305. In the dewatering unit 317, water is
7 distilled from the reactants in dewatering tower 310. Rising vapor exits via line 311a and
8 passes through heat exchanger 312 wherein condensation occurs. Effluent from heat
9 exchanger 312 is advanced to water trap 318 via line 311b. Water is removed from water trap
10 318 via line 313, with the bottom organic layer being returned to the dewatering tower 310.
11 Dewatered reactants may be removed via line 316 and conveyed to either line 316a or line
12 316b. Some of the dewatered reactant may be withdrawn by conduit 314b, sent through heat
13 exchanger 315 and returned to the tower 310 via line 314a. In this regard, heat exchanger 315
14 may serve as a reboiler.

30

35

40

45

15
16 After reaction in either reactor 320 or 321, LAB product is sent to lines 322 and 331
17 from either line 322a or 322b after passing through heat exchanger 323. When desired, one
18 of the catalyst beds may be regenerated, as by calcination for example, through use of
19 regeneration heater 350, which may be connected to the reactor of choice by dotted line 351
20 through valving and hardware that are not shown. The reactors 320 and 321 may optionally
21 be run simultaneously. The reactors 320 and 321 may be loaded with mordenite catalyst in
22 any fashion, as would be apparent to one of skill in the art. Typically, a plugged flow
23 arrangement is used. The amount of catalyst employed may vary depending on a variety of
24 considerations such as type and flow rate of reactants, temperature and other variables. The
25 combined effluents from conventional reactor 330 and mordenite reactors 320 or 321 may be
26 fed to a second conventional reactor 340, or optionally may be sent to a purification section
27 directly if no unreacted paraffin is present (the conventional reactor serves to complete
28 reaction of any paraffin that is not converted in the mordenite reactors 320, 321). In FIG. 4,
29 effluent from the second conventional alkylation reactor is advanced to a purification section.

50

55

5

-17-

1 The second alkylation reactor may be used to react unreacted feed stock from reactors 330,
2 320 and 321 to thereby reduce recycle loads.

10

3
4 It should be appreciated that a wide variety of configurations are contemplated, and
5 the figures should not be construed as limiting this invention or claims hereto. Additional
6 reactors and other equipment may, for example, be used.

15

7
8 The following examples are illustrative of the present invention and are not intended to
9 be construed as limiting the scope of the invention or the claims. Unless otherwise indicated, all
10 percentages are by weight. In the examples, all reactants were commercial grades and used as
11 received. The apparatus depicted in FIG. 1 was employed for examples 2-4. The apparatus
12 depicted in FIG. 1 was used for example 5.

20

25

30

35

40

45

50

55

13
14 It may be noted that example 2 illustrates LAB production from paraffin dehydrogenate
15 using the fluoride-treated mordenite catalyst of example B, where good catalyst life (250+ hrs)
16 is achieved without catalyst regeneration, while maintaining a 2-phenyl LAB selectivity of
17 >70% and high LAB productivity without significant loss of fluoride. Comparative example 1,
18 on the other hand, using untreated mordenite, with no fluoride added, shows a rapid decline in
19 LAB production. In addition, examples 3 and 4 illustrate LAB production using a 5:1 molar
20 benzene/C₁₀-C₁₄ paraffin feed mix and the fluoride-treated mordenite catalysts of Example B
21 when operating at different LHSV's in the range of 0.2-0.4 hr⁻¹. Catalyst life may exceed 500
22 hours. Example 5 illustrates LAB production with the fluoride-treated mordenite catalyst where
23 the alkylation is conducted at higher temperatures and under pressure. Examples 6-8 illustrate
24 the performance of three HF-treated mordenite catalysts with different fluoride loadings.
25 Example 9 shows how virtually no alkylation activity is observed with a highly-fluorinated
26 mordenite.

27

5

-18-

1

EXAMPLE A

2

10

This example illustrates the preparation of a hydrogen fluoride-modified mordenite.

4

15

To 30 g of acidified mordenite (LZM-8, SiO₂/Al₂O₃ ratio 17; Na₂O wt% 0.02, surface area 517 m²/g, powder, from Union Carbide Corp.) was added 600 ml of 0.4% hydrofluoric acid solution, at room temperature. After 5 hours the solid zeolite was removed by filtration, washed with distilled water, dried at 120°C overnight, and calcined at 538°C.

9

20

EXAMPLE B

11

The example illustrates the preparation of a hydrogen fluoride-modified mordenite.

13

25

To 500 g of acidified, dealuminized, mordenite (CBV-20A from PQ Corp.: SiO₂/Al₂O₃ molar ratio 20; Na₂O, 0.02 wt%; surface area 550 m²/g, 1/16" diameter extrudates, that had been calcined at 538°C, overnight) was added a solution of 33 ml of 48% HF solution in 1633 ml of distilled water, the mix was cooled in ice, stirred on a rotary evaporator overnight, then filtered to recover the extruded solids. The extrudates were further washed with distilled water, dried in vacuo at 100°C, and then calcined at 538°C, overnight.

30

Analyses of the treated mordenite showed:

35

F: 1.2%

Acidity: 0.49 meq/g

23

EXAMPLE I

25

40

This example illustrates the preparation of linear alkylbenzenes using a hydrogen fluoride-modified mordenite catalyst.

28

45

To a 500 mL flask, fitted with condenser and Dean Stark Trap was added 100 mL of benzene (reagent grade) plus 10 g of hydrogen fluoride-modified mordenite zeolite, prepared by

50

55

5

-19-

10

1 the method of Example A. The mix was refluxed for 15-20 minutes to remove small amounts
 2 of moisture, then a combination of benzene (50 ml) plus 1-dodecene (10 g) was injected into the
 3 flask and the solution allowed to reflux for 3 hours.

15

4

5 Upon cooling, the modified mordenite catalyst was removed by filtration, the filtrate
 6 liquid flashed to remove unreacted benzene, and the bottoms liquid analyzed by gas
 7 chromatography.

20

8

9 Typical analytical data are summarized in Table 1.

10 TABLE I

DODECENE CONV. (%)	LAB ISOMER DISTRIBUTION (%)					HEAVIES (%)	LINEAR LAB (LLAB) (%)
	2-Ph	3-Ph	4-Ph	5-Ph	6-Ph		
99.7	79.9	16.5	0.8	1.3	1.3	0.2	95.9

25

13
14
15 EXAMPLE 2
16

30

17 This example illustrates the preparation of linear alkylbenzenes from paraffin
 18 dehydrogenate using a hydrogen fluoride-treated mordenite catalyst.

35

19

20 In the example, benzene was alkylated with a sample of C₁₀-C₁₄ paraffin dehydrogenate
 21 containing about 8.5% C₁₀-C₁₄ paraffins. Alkylation was conducted in a process unit as shown
 22 in FIG. 1.

40

23

24 Alkylation was conducted by first charging 500 ml of a benzene/paraffin dehydrogenate
 25 mix (10:1 molar ratio, benzene/C₁₀-C₁₄ paraffin) to the reboiler and 250 cc of the HF-treated
 26 mordenite of example B to the 1.1" i.d. reaction zone. The mordenite was held in place using
 27 Goodloe packing. The reboiler liquid was then heated to reflux and a benzene plus C₁₀-C₁₄
 28 paraffin dehydrogenate mix (10:1 molar ratio, benzene/C₁₀-C₁₄ paraffin) continuously
 29 introduced into the unit above the catalyst column at the rate of 100 cc/hr. (LHSV=0.4 hr⁻¹).
 30

50

55

5

-20-

10

Under steady state, reflux, conditions liquid product was continuously withdrawn from the reboiler and water continuously taken off from the water trap. The crude liquid product was periodically analyzed by gas chromatography. The reboiler temperature was typically in the controlled range of 97-122°C. The column head temperature variability was 78-83°C. A summary of the analytical results may be found in Table 2.

15

After 253 hours on stream, the recovered HF-treated mordenite catalyst showed by analysis:

20

9	F:	1.1%
10	Acidity:	0.29 meq/g
11	H ₂ O:	0.3%

12

13

Table 2

25

Time on Stream (Hrs)	Sample	Alkylate Conc. (%)	2-Phenyl Sel. (%)	C ₆ H ₆ Conc. (%)
0	0	1.4		32.3
2	1	3.4		19.7
4	2	5.8	74.9	16.6
6	3	6.6	75.8	25.2
32	4	7.9	80.7	27.0
56	5	7.8	82.7	27.0
69	6	7.3	81.4	27.4
94	7	6.5	82.0	27.8
118	8	6.0	78.4	27.7
142	9	5.9	81.3	26.9
166	10	5.4	81.5	27.3
207	11	5.3	81.3	26.1
229	12	5.1	81.1	27.4
253	13	4.9	81.4	28.1

40

45

50

55

5

-21-

1 Comparative Example 1

2

10

3 This example illustrates the preparation of linear alkylbenzene from paraffin
4 dehydrogenate using an untreated mordenite catalyst.

5

15

6 Following the procedures of Example 9, the alkylation unit was charged with 250 cc of
7 untreated, calcined, mordenite, (the starting mordenite of Example B), and the liquid feed
8 comprised benzene plus C₁₀-C₁₄ paraffin dehydrogenate mix in a 10:1 molar ratio of
9 benzene/C₁₀-C₁₄ paraffin.

10

20

11 Typical results are summarized in Table 3.

12

13 The recovered mordenite showed by analysis:

25

14 Acidity: 0.29 meq/g

15 H₂O: 2.1%

16

30

35

40

45

50

55

5

-22-

1

Table 3

Time on Stream (Hrs)	Sample	Alkylate Conc. (%)	2-Phenyl Sel. (%)	C ₆ H ₆ Conc. (%)
0	0			11.2
2	1	6.50		9.9
4	2	7.16	73.2	17.1
6	3	7.09	73.1	26.4
22	4	8.61	73.9	26.6
31	5	10.49	67.4	15.8
46	6	7.39	75.0	27.7
70	7	6.39	75.1	28.5
93	8	6.08	73.6	23.0
144	9	5.21	73.6	15.8
157	10	4.40	73.9	26.2
180	11	3.06	69.6	27.1
204	12	1.32		19.5
228	13	1.32		33.3

10

15

20

25

30

2

3

4

5

35

6

This example also illustrates the preparation of linear alkylbenzene from paraffin dehydrogenate using a hydrogen fluoride-treated mordenite catalyst.

8

40

9

Following the procedures of Example 2, the alkylation unit was charged with 250 cc of the HF-treated mordenite of Example B, and the liquid feed comprised a benzene plus C₁₀-C₁₄ paraffin dehydrogenate mix in a 5:1 molar ratio of benzene/C₁₀-C₁₄ paraffin, the reboiler temperature was typically in the range of 122-188°C, the column head temperature 78-83°C.

45

Typical analytical results are summarized in Table 4.

14

50

55

5

-23-

1 After 503 hours on stream, the recovered HF-treated mordenite catalyst showed on
2 analysis:

10

3 F: 1.0%

4 Acidity: 0.35 meq/g

5 H₂O: 0.1%

6

15

7

8

20

25

30

35

40

45

50

55

5

-24-

1
2

Table 4

Time on Stream (Hrs)	Sample	Alkylate Conc. (%)	2-Phenyl Sel. (%)	C ₆ H ₆ Conc. (%)	Corrected* Alkylate Conc. (%)
0	0	1.0		8.9	1.1
2	1	3.5	61.8	0.3	3.5
4	2	7.1	72.1	0	7.1
6	3	6.8	76.7	7.2	7.3
34	4	8.4	79.7	14.3	9.8
71	5	7.2	81.8	14.6	8.5
96	6	6.5	80.8	15.5	7.7
119	7	6.3	80.6	15.1	7.4
643	8	6.0	81.0	14.3	7.0
168	9	5.9	80.7	14.4	6.9
239	10	5.0	78.2	8.8	5.5
263	11	5.3	79.2	13.5	6.2
288	12	5.0	79.6	16.5	6.0
311	13	5.4	79.4	4.1	5.6
335	14	5.5	79.2	8.2	6.0
408	15	4.9	79.4	13.1	5.6
432	16	4.7	78.8	14.4	5.5
456	17	4.4	78.5	14.1	5.1
479	18*	4.7	78.6	2.7*	4.8
488	19†	4.9	78.5	2.4‡	5.0
503	20*	5.1	78.9	0.6‡	5.1

3

4 * Corrected for benzene in effluent sample.

5 † Applied pressure 8" H₂O6 ‡ Applied pressure 12" H₂O

45

7

8

50

55

5

-25-

1

Example 4

2

10

3 This example also illustrates the preparation of linear alkylbenzenes from paraffin
4 dehydrogenate using a hydrogen fluoride-treated mordenite catalyst.

5

15

6 Following the procedures of Example 2, alkylation was conducted in the glassware unit
7 of FIG. 1 complete with catalyst column, reboiler, condenser and controls. To the reaction zone
8 was charged 500 cc of HF-treated mordenite of Example B. The liquid feed comprised a
9 benzene plus C₁₀-C₁₄ paraffin dehydrogenate mix in a 5:1 molar ratio of benzene /C₁₀-C₁₄
10 paraffin. The feed rate was 100 cc/hr (LHSV:0.2 hr⁻¹).

20

11

12 Under typical steady state, reflux, conditions, with a reboiler temperature range of 131-
13 205°C and a head temperature of 76-83°C, typical results are summarized in Table 5.

25

30

35

40

45

50

55

5

-26-

1

Table 5

	Pressure (Inch H ₂ O)	Reboiler Temp. (°C)	Time on Stream (Hrs)	Sample	Alkylate Conc. (%)	2-Phenyl Sel. (%)	C ₁₁ I ₁ Conc. (%)	Corrected ^a Alkylate Conc. (%)
10	12	205	2	1	8.2	74.3	0.5	8.3
		193	4	2	9.2	75.0	0.4	9.2
		175	6	3	10.0	74.8	2.3	10.3
15		204	21	4	12.7	78.7	0.3	12.7
		146	44	5	11.7	81.0	10.4	12.9
		136	68	6	11.5	81.8	10.0	12.7
			2-3 days	C ^b	11.6	81.4	9.4	12.7
20		136	93	7	11.3	82.6	10.8	12.5
			4-5 days	C-1 ^c	11.0	81.8	11.0	12.2
		142	165	8	10.4	83.0	11.4	11.5
25		142	189	9	10.2	83.4	10.5	11.2
		145	213	10	9.7	80.2	11.2	10.7
		139	238	11	9.6	83.4	11.1	10.7
		143	261	12	9.9	81.9	11.0	11.0
30		133	332	13	9.2	83.4	11.3	10.3
		138	356	14	8.9	83.5	11.1	9.9
		138	381	15	8.8	83.0	11.3	9.8
		131	405	16	8.7	82.8	11.2	9.7

2 ³ Corrected for benzene in effluent sample3 ⁴ Composite product

5

6

7

EXAMPLE 5

8

9 This example illustrates the preparation of linear alkylbenzenes from paraffin
10 dehydrogenate using a hydrogen fluoride-treated mordenite catalyst.

11

12

13 Following the procedures of Example 2, alkylation of benzene with C₁₀-C₁₄ paraffin
dehydrogenate was conducted using the stainless-steel unit of FIG. 2, complete with catalyst

50

55

5

-27-

10

1 column, reboiler, condenser, and controls. About 250 cc of HF-treated mordenite of Example B
2 was charged to the column. The liquid feed comprised benzene plus C₁₀-C₁₄ paraffin
3 dehydrogenate mix in a 10:1 molar ratio of benzene/C₁₀-C₁₄ paraffin. The LHSV varied from
4 0.2 to 0.4 hr⁻¹.

15

5

6 Alkylation was conducted over a range of column and reboiler temperatures and a range
7 of exit pressures. Typical results are summarized in Table 6.

8

9

10

20

25

30

35

40

45

50

55

5

-28-

1

Table 6

10	Column Temp (°C)	Pressure		Pot Temp. (°C)	Time (hr)	Sample (#)	Alkylate Conc. (%)	2- Phenyl Sel. (%)	C ₆ H ₆ Conc. (%)
		DIFF (psi)	EXIT (psi)						
	149-129	0.1	0	188	4	1	3.3		6.3
	152-126	0	0	200	20	2	1.8		32.7
15	195-108	0	0	199	25	3	5.7		8.7
	218-111	0	0	201	28	4	0.8		67.5
	212-118	0	0	201	44	5	8.5	71.7	4.5
20	209-114	0.2	0	198	52	6	2.4		47.3
	228-116	0	0	197	68	7	6.9	72.6	12.4
	187-107	0.5	0	197	76	8	2.9	74.6	44.1
				76		9 ^a	4.5	72.9	25.3
						9C ^b	6.5	72.2	1.0
25	174-107	0	0	178	6	10	4.1	79.2	54.9
	170-106	0	0	172	22	11	2.0		59.8
					28	12 ^c	6.5	76.8	26.8
30	142-107	0	0	136	31	13	4.8	67.9	18.9
	141-110	0	0	138	47	14	4.4	65.9	16.9
	142-110	0	0	136	55	15	5.0	63.9	16.6
	168-111	0	0	131	71	16	4.1	64.8	16.7
35	170-108	0	0	150	79	17	5.0	72.0	8.8
	175-113	0	0	143	95	18	5.9	68.1	15.2
	145-106	0	5.2	188	14	19	3.2	60.2	9.0
	149-108	0	4.2	186	20	20	4.8	66.3	12.0
40	160-118	0	11.7	213	29	21	4.2		6.7
	160-119	0	9.3	210	44	22	5.2		6.6

2

^aComposite product

3

^bStripped composite product

4

5

6

45

50

55

5

-29-

1

EXAMPLES 6-8

2

10

3 These examples illustrate the preparation of linear alkylbenzene using hydrogen
4 fluoride-modified mordenite catalysts with different fluoride treatment levels.

5

15

6 Following the procedures of Example 1, the alkylation unit was charged with benzene
7 (100 ml), a 10 g sample of hydrogen fluoride-modified mordenite prepared by the procedure of
8 Example B, plus a mix of benzene (50 ml) and 1-decene (10 g). Three HF-treated mordenites
9 were tested, having the composition:

10

11

Catalyst "C" 0.25% IIF on mordenite (CBV-20A)

12

Catalyst "D" 0.50% IIF on mordenite (CBV-20A)

13

Catalyst "E" 1.0% HF on mordenite (CBV-20A)

14

15

In each experiment samples of the bottoms liquid fraction were withdrawn at regular
16 periods and subject to gas chromatography analyses. The results are summarized in Table 7.

17

30

18

19

35

40

45

50

55

5

-30-

1

Table 7

	CATALYST	TIME	%LLAB	%ISOS	%HVY	%2Ph	%3Ph	%4Ph	%5Ph	%6&7Ph
10	D	10	11.75	0.14	0	73.36	21.87	2.89	0.94	1.02
		20	12.43	0.21	0	72.97	21.96	3.14	1.13	0.81
		30	12.88	0.21	0	72.67	22.13	3.03	1.16	1.01
		40	12.27	0.22	0	73.02	21.92	2.85	1.06	1.14
		50	12.15	0.98	0	72.46	21.67	3.21	1.17	1.49
		50	12.24	1.01	0	72.53	21.63	3.23	1.12	1.44
20		60	12.28	0.21	0	72.96	22.07	2.93	1.14	0.91
		60	11.98	0.21	0	72.97	22.21	2.93	1.17	0.83
		C	12.2	0.18	0	72.54	22.46	3.21	0.98	0.82
		20	12.7	0.39	0	71.51	22.61	2.91	1.02	2.13
25		30	12.52	0.21	0	71.96	22.68	2.96	1.04	1.36
		40	12.75	0.21	0	71.84	22.67	3.22	1.02	1.25
		50	12.98	0.21	0	71.57	22.81	3.16	1.08	1.39
		60	12.54	0.21	0	71.45	22.81	3.19	1.12	1.44
		60	12.33	0.21	0	71.61	22.87	2.92	1.05	1.31
40	E	10	10.56	0.05	0	75.19	19.41	2.18	3.22	
		20	12.95	0.15	0	74.36	19.23	3.01	3.4	
		30	13.44	0.18	0	74.11	19.42	3.2	3.27	
		40	13.16	0.15	0	074.16	19.38	3.12	3.34	
		50	13.1	0.15	0	74.43	19.16	3.21	3.28	
		60	12.83	0.15	0	74.28	19.49	2.88	3.35	

50

55

5

-31-

10

CATALYST	TIME	%LLAB	%ISOS	%HVY	%2Ph	%3Ph	%4Ph	%5Ph	%6&7Ph
	60	12.87	0.16	0	73.82	19.97	2.8	3.2	

1

2

3

Example 9

4

15

5 This example illustrates the inactivity of a heavily loaded hydrogen-fluoride modified
6 mordenite catalyst.

7

20

8 Following the procedures of Example 2, the alkylation unit was charged with 100 cc of
9 a hydrogen fluoride-treated mordenite (CBV-20A) prepared by the method of Example B but
10 having a much higher loading of HF (fluoride content 4.8%). The acidity of said HF-treated
11 mordenite was 0.15 meq/g.

25

12 No significant amount of alkylated product was detected by gas chromatography.

13

14

15

30

16

17

35

40

45

50

55

Claims

5

10

15

20

25

30

35

40

45

50

55

5

-32-

1 What is Claimed Is:

2

10

3 1. A process for the production of linear alkylbenzene, comprising:
4 contacting benzene and an paraffin having about 8 to about 30 carbons in the presence
5 of a fluorine-containing mordenite to form a first linear alkylbenzene stream;
6 contacting benzene and an paraffin having about 8 to about 30 carbons in the presence
7 of a conventional linear alkylbenzene alkylation catalyst to form a second linear alkylbenzene
8 stream;
9 combining the first linear alkylbenzene stream and the second linear alkylbenzene
10 stream form a third linear alkylbenzene stream.

20

11

12 2. The process of claim 1, wherein the paraffin is obtained by dehydrogenating a
13 paraffin.

14

25

15 3. The process of claim 1, wherein the third linear alkylbenzene stream is distilled to
16 remove unreacted benzene, paraffin and any components heavier than the linear
17 alkylbenzene.

30

18

35

19 4. The process of claim 1, wherein the fluorine-containing mordenite is made by
20 contacting mordenite with an aqueous hydrogen fluoride composition having a hydrogen
21 fluoride concentration in the range from about 0.1 percent by weight to about 1 percent by
22 weight.

23

40

24 5. The process of claim 1, wherein the fluorine-containing mordenite has a silica to
25 alumina molar ratio in a range from about 10:1 to about 50:1, wherein the mordenite has been
26 treated by contacting mordenite with an aqueous hydrogen fluoride solution, wherein the
27 hydrogen fluoride in the aqueous solution has a concentration percent by weight.

28

45

50

55

5

-33-

10

1 6. The process of claim 1, wherein the benzene and paraffin that is contacted with
2 mordenite is a slip stream from a stream containing benzene and paraffin that is to be contacted
3 with the conventional alkylation catalyst.

15

4
5 7. The process of claim 1 which is operated under conditions effective to produce a 2-
6 phenyl isomer content in the third linear alkylbenzene stream in the range from about 30 to
7 about 40 percent by weight.

20

8
9 8. The process of claim 1, wherein the benzene and paraffin to be contacted with the
10 mordenite has a benzene/paraffin ratio of from about 2:1 to about 20:1, wherein the mordenite is
11 maintained at a temperature in the range from about 70 degrees Centigrade to about 200 degrees
12 Centigrade, and wherein the benzene and paraffin that contacts the mordenite has a combined
13 liquid hourly space velocity in the range from about 0.05 hr⁻¹ to about 10 hr⁻¹.

25

14
15 9. The process of claim 1 wherein the conventional linear alkylbenzene alkylation catalyst
16 is hydrogen fluoride.

17

30

18 10. The process of claim 1 wherein the conventional linear alkylbenzene alkylation catalyst
19 is aluminum chloride.

20

35

21 11. A linear alkylbenzene composition having a 2-phenyl isomer content in the range
22 from about 30 to about 40 percent by weight, wherein the linear alkylbenzene composition is
23 obtained by

40

24 contacting benzene and an paraffin having about 8 to about 30 carbons in the presence
25 of a fluorine-containing mordenite to form a first linear alkylbenzene stream;

26 contacting benzene and an paraffin having about 8 to about 30 carbons in the presence
27 of a conventional linear alkylbenzene alkylation catalyst to form a second linear alkylbenzene
28 stream;

45

29 combining the first linear alkylbenzene stream and the second linear alkylbenzene
30 stream to form the linear alkylbenzene composition.

50

55

5

-34-

1

10 12. The composition of claim 11 wherein the fluorine-containing mordenite is made by
3 contacting mordenite with an aqueous hydrogen fluoride composition having a hydrogen
4 fluoride concentration in the range from about 0.1 percent by weight to about 1 percent by
5 weight.

6

15 13. A process useful for the production of linear alkylbenzene, comprising:
8 combining a product from a conventional linear alkylbenzene alkylation reactor with a
9 product from a linear alkylbenzene alkylation reactor containing fluorine-containing
10 mordenite.

20

11

25 14. The process of claim 13 wherein the product from the conventional linear
13 alkylbenzene alkylation reactor has a 2-phenyl isomer content below about 30 percent by
14 weight and wherein the product of the mordenite reactor has a 2-phenyl isomer content above
15 about 70 percent by weight.

16

30 17. The process of claim 13 wherein the conventional linear alkylbenzene alkylation
18 reactor is a hydrogen fluoride reactor.

19

35 20 16. The process of claim 13 wherein the conventional linear alkylbenzene alkylation
21 reactor is an aluminum chloride reactor.

22

40

23 17. The process of claim 13 wherein the fluorine-containing mordenite is made by
24 contacting mordenite with an aqueous hydrogen fluoride composition having a hydrogen
25 fluoride concentration in the range from about 0.1 percent by weight to about 1 percent by
26 weight.

27

45

28 18. A process for the production of linear alkylbenzene, comprising:
29 dehydrogenating a paraffin to form an paraffin;

50

55

5

-35-

- 1 sending a primary feed stream of benzene and the paraffin through a conduit to a
- 2 conventional linear alkylbenzene alkylation reactor;
- 3 contacting the primary feed stream in the conventional linear alkylbenzene alkylation
- 4 reactor with a conventional linear alkylbenzene alkylation catalyst under conditions effective
- 5 to react the benzene and paraffin to form a first linear alkylbenzene product;
- 6 withdrawing a portion of the primary feed stream from the conduit and contacting the
- 7 portion with a fluorine-containing mordenite under conditions effective to react the benzene
- 8 and paraffin to form a second linear alkylbenzene product;
- 9 combining the first and second linear alkylbenzene products to form a crude linear
- 10 alkylbenzene stream;
- 11 distilling the crude linear alkylbenzene stream in a first distillation column to separate
- 12 benzene that did not react and to form a benzene-free linear alkylbenzene stream;
- 13 optionally distilling the benzene-free linear alkylbenzene stream in a second
- 14 distillation column to separate any paraffin and to form a linear alkylbenzene stream;
- 15 distilling the second paraffin free alkylbenzene stream in a third distillation column to
- 16 provide an overhead of a purified linear alkylbenzene product and removing a bottoms stream
- 17 containing any heavies.

18

- 19 19. The process of claim 18 further comprising recycling the benzene from distillation of
- 20 the crude linear alkylbenzene stream to the conduit.

21

- 22 20. The process of claim 18 further comprising recycling any distilled paraffin to the
- 23 dehydrogenating step.

24

- 25 21. The process of claim 18 further comprising dewatering the portion of the primary feed
- 26 stream prior to contact with the fluorine-containing mordenite.

27

- 28 22. The process of claim 18 wherein the conventional linear alkylbenzene alkylation
- 29 catalyst is a hydrogen fluoride.

30

50

55

5

-36-

1 23. The process of claim 18 wherein the conventional linear alkylbenzene alkylation
2 catalyst is aluminum chloride.

10

3 4 24. The process of claim 18 wherein the fluorine-containing mordenite is made by
5 contacting mordenite with an aqueous hydrogen fluoride composition having a hydrogen
6 fluoride concentration in the range from about 0.1 percent by weight to about 1 percent by
7 weight.

15

8

20

25

30

35

40

45

50

55

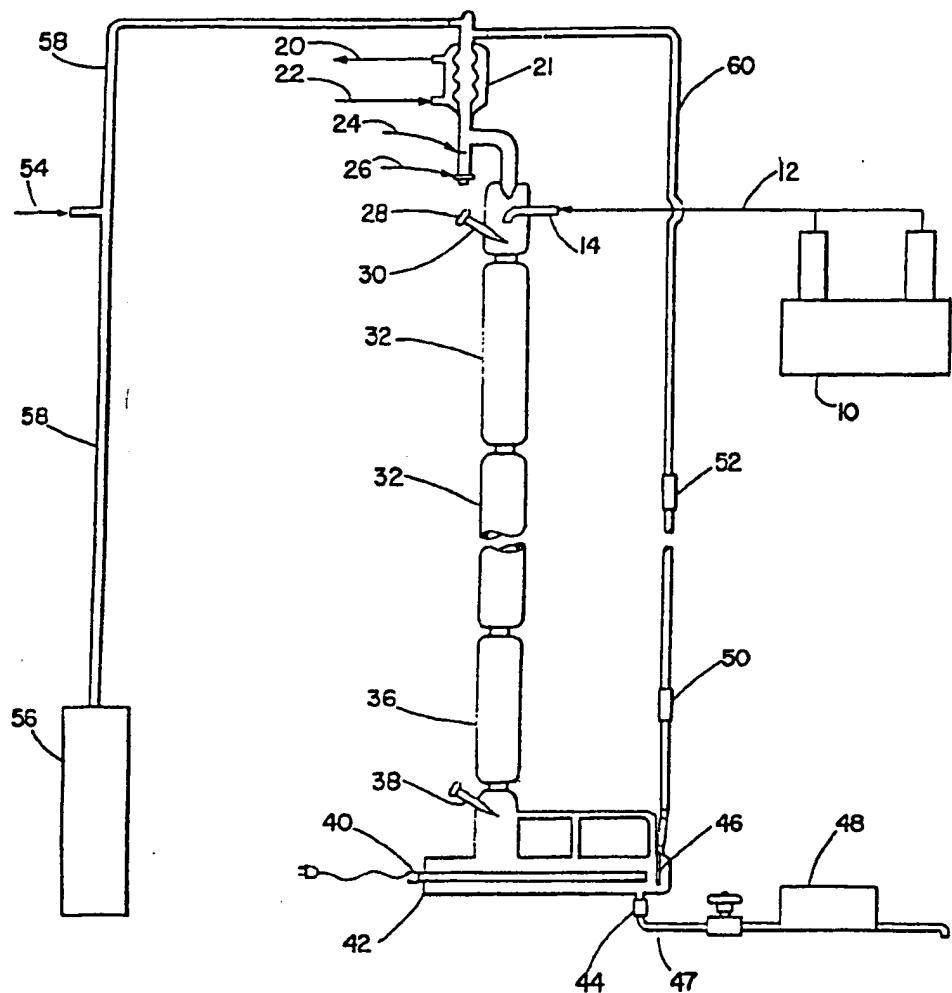


Fig. 1

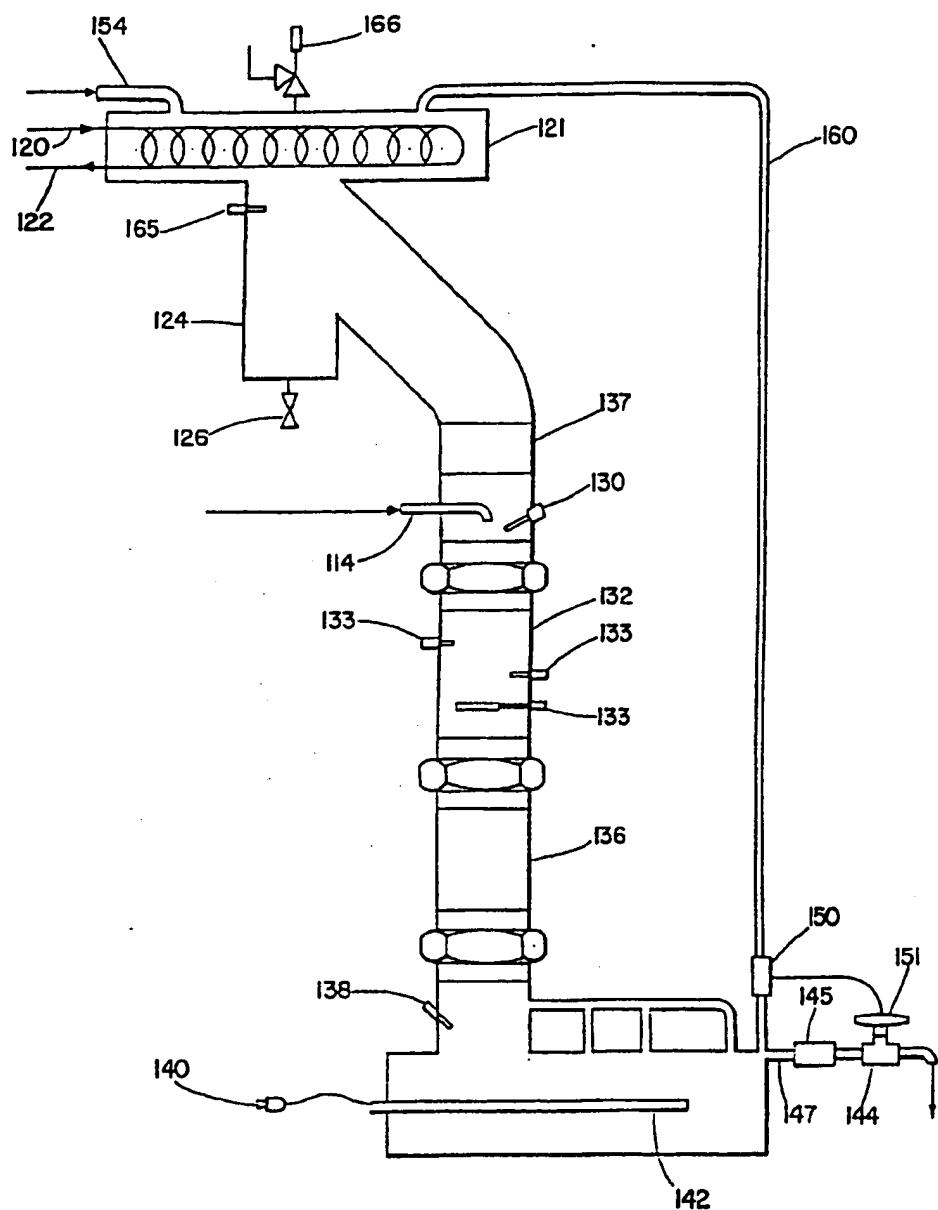


Fig. 2

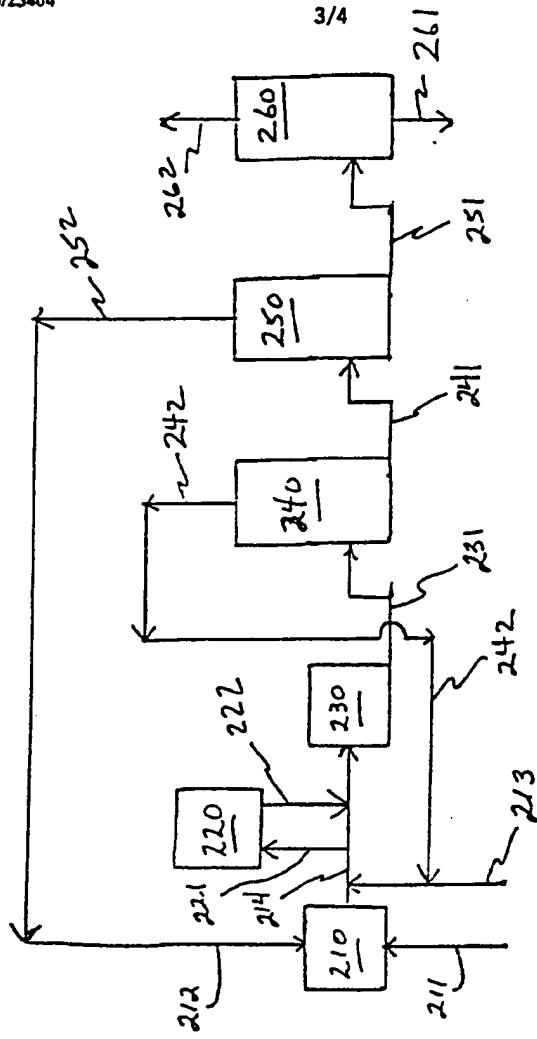


FIG. 3

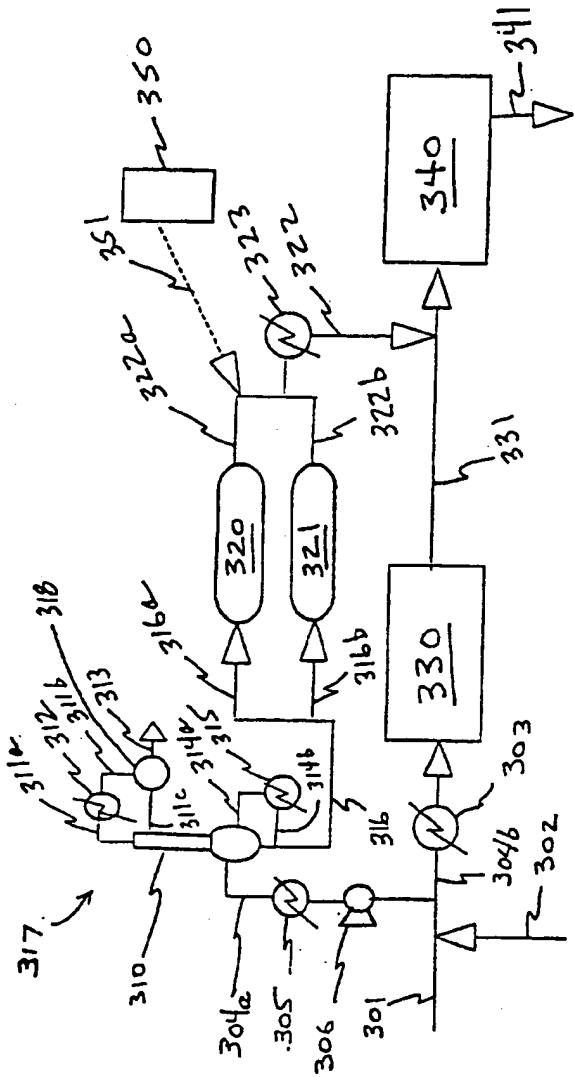


FIG. 4

INTERNATIONAL SEARCH REPORT

Int. Appl. No.
PCT/US 99/24274

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C07C15/107 C07C2/66		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C07C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 47573 A (HUNTSMAN PETROCHEMICAL CORP) 18 December 1997 (1997-12-18) claims page 3 -page 11 -----	1, 2, 4-24
A	US 5 276 231 A (KOCAL JOSEPH A ET AL) 4 January 1994 (1994-01-04) claims -----	2
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "T" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the International search 27 January 2000		Date of mailing of the International search report 07/02/2000
Name and mailing address of the ISA European Patent Office, P.B. 5010 Patentaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2640, Tx. 31 651 epo nl, Fax. (+31-70) 340-3018		Authorized officer Van Geyt, J

INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US 99/24274**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
See FURTHER INFORMATION sheet PCT/ISA/210

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international applicant, as follows:

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.
 No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 99 24274

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Contrary to the requirements of Rule 10.1(e) PCT, the word "paraffin" is used with two different and contradictory meanings, namely the generally accepted meaning "alkane" and another, unusual, as synonym of "alkene". Claim 2 appears contradictory as these different meanings are used in a single sentence. For search purposes, the correct meanings depending on the context have been used. This interpretation is based on the third paragraph of page 8.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 99/24274

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9747573 A	18-12-1997	US 5777187 A CA 2257249 A. EP 0918736 A	07-07-1998 18-12-1997 02-06-1999
US 5276231 A	04-01-1994	NONE	